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# RADIOLYTIC REDUCTION OF TETRAVALENT CERIU IN THE PRESENCE OF MONOVALENT THALLIUM UNDER IRRADIATION AT HIGH DOSAGE RATES

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We have shown earlier [1-3] that overlapping of the tracks of ionizing particles in irradiation at dosage rates of approximately  $10^{21}$  ev/ml·sec, or higher, alters the yield of radical and molecular products from the radiolysis of water and thereby leads to a marked diminution in the yield of  $\text{Fe}^{3+}$  in irradiation of aqueous sulfuric acid solutions of ferrous sulfate in air and to an increase in the yield of  $\text{Ce}^{3+}$  in irradiation of aqueous sulfuric acid solutions of ceric sulfate. The study of the effect of high dosage rates on the course of radiolytic transformations in aqueous solutions has been extended by investigating the radiochemical processes in sulfuric acid solutions of mixed  $\text{Ce}^{4+}$  and  $\text{Tl}^{+}$  sulfates at dosage rates ranging up to approximately  $10^{23}$  ev/ml·sec.

These high dosage rates were obtained through single monoenergetic pulses of 0.8 Mev electrons which were produced in the accelerating tube of a linear accelerator [2, 3]. The experimental technique and method of measuring the dosage rate have been described in our previous communications [2, 3]. Doubly distilled water was used in each experiment. The following reactants were employed: ceric sulfate ("pure" grade) recrystallized from doubly distilled water to which a small amount of sulfuric acid had been added; thallous sulfate (analytical grade) recrystallized from doubly distilled water; cerous sulfate (analytical grade) and sulfuric acid

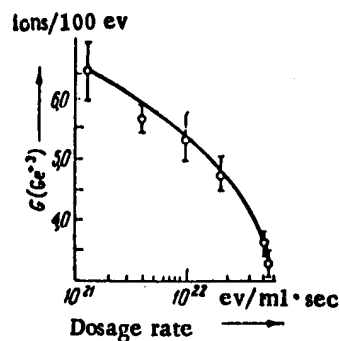


Fig. 1. The relation between  $G(\text{Ce}^{3+})$  and dosage rate in the  $\text{Ce}^{4+} - \text{Tl}^{+}$  system ( $\text{Ce}^{4+}$  concentration,  $2 \cdot 10^{-4}$  M;  $\text{Tl}^{+}$  concentration,  $10^{-2}$  M).

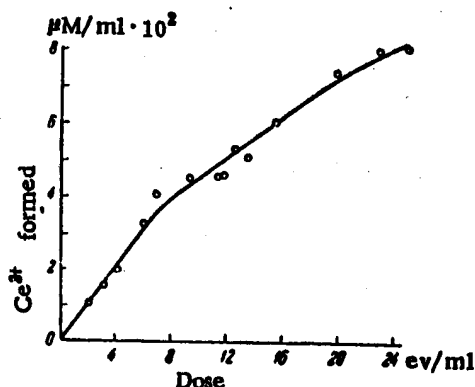


Fig. 2. The relation between the reduction of  $\text{Ce}^{4+}$  in the presence of  $10^{-2}$  M  $\text{Tl}^{+}$  and the dose at a dosage rate of  $5 \cdot 10^{22}$  ev/ml·sec.

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(chemically pure grade), neither of which were subjected to preliminary purification. These solutions were irradiated in a glass cell with a glass membrane approximately 80  $\mu$  thick. The irradiated volume was 7 ml and the depth of the liquid layer, 5 mm.

The amount of  $\text{Ce}^{3+}$  formed by irradiation was determined spectrophotometrically. The molar extinction coefficient of  $\text{Ce}^{4+}$  in 0.8 N  $\text{H}_2\text{SO}_4$  was assumed to be equal to 5580 at 320  $\text{m}\mu$  [4]. The  $\text{Ti}^{3+}$  was determined indirectly. The amount of  $\text{Ce}^{4+}$  in the irradiated solution was first determined spectrophotometrically and a  $10^{-3}$  M solution of Mohr's salt in 0.8 N  $\text{H}_2\text{SO}_4$  then added. A certain amount of  $\text{Fe}^{2+}$  was oxidized by the  $\text{Ti}^{3+}$  and the  $\text{Ce}^{4+}$ . Knowing the amount of  $\text{Ce}^{4+}$  in the solution, the  $\text{Ti}^{3+}$  content could be obtained from a spectrophotometric determination of the  $\text{Fe}^{3+}$  concentration. This method proved to be satisfactory for irradiation at dosage rates up to about  $10^{22}$   $\text{ev/ml}\cdot\text{sec}$ . It was not sufficiently precise at higher dosage rates where the  $\text{Ti}^{3+}$  concentration was very low.

Use was made of an air-saturated 0.8 N sulfuric acid solution containing  $2\cdot 10^{-4}$  M  $\text{Ce}^{4+}$  and  $10^{-3}$  M  $\text{Ti}^{3+}$  in studying the effect of high dosage rates on the  $G(\text{Ce}^{3+})$  value for mixed  $\text{Ce}^{4+} - \text{Ti}^{3+}$  solutions. The value of  $G(\text{Ce}^{3+})$  for  $\text{Co}^{60}$   $\gamma$ -irradiation at dose rates of  $2.5\cdot 10^{15}$   $\text{ev/ml}\cdot\text{sec}$  is 7.9 ions/100  $\text{ev}$  [5] and is independent of the  $\text{Ti}^{3+}$  concentration over the range from  $10^{-3}$  to  $10^{-5}$  M. Our experiments on the irradiation of mixed  $\text{Ce}^{4+} - \text{Ti}^{3+}$  solutions of the concentration indicated with a continuous electron current of 0.9 Mev and a dose rate of  $9.4\cdot 10^{15}$   $\text{ev/ml}\cdot\text{sec}$  gave a value of  $G(\text{Ce}^{3+})$  of  $7.6 \pm 0.2$  ions/100  $\text{ev}$ . The slight difference between this result and the value of [5] obviously arises from the fact that our dosage rate was greater by a factor of four.

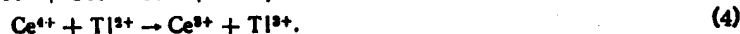
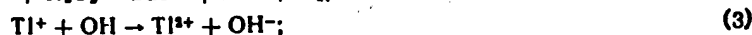
There was a pronounced diminution in the value of  $G(\text{Ce}^{3+})$  with increasing dose rate in electron pulse irradiation of  $\text{Ce}^{4+} - \text{Ti}^{3+}$  solutions. The results are presented in Fig. 1. The  $\text{Ce}^{4+} - \text{Ti}^{3+}$  solutions were irradiated with from 1 to 50 electron pulses, depending on the dosage rate.\* Each value of  $G(\text{Ce}^{3+})$  represents the mean of 5-15 measurements.

Figure 2 shows the relation between the formation of  $\text{Ce}^{3+}$  in 0.8 N sulfuric acid solution with  $2\cdot 10^{-4}$  M  $\text{Ce}(\text{SO}_4)_2$  and  $10^{-3}$  M  $\text{Ti}_2\text{SO}_4$  and the dosage in impulse irradiation at a dose rate of  $5\cdot 10^{22}$   $\text{ev/ml}\cdot\text{sec}$ . The value of  $G(\text{Ce}^{3+})$  is somewhat dependent on the initial  $\text{Ti}^{3+}$  concentration at the high dosage rates. It is to be seen from Fig. 3 that  $G(\text{Ce}^{3+})$  rises with increasing  $\text{Ti}^{3+}$  concentration and is proportional to the logarithm of the  $\text{Ti}_2\text{SO}_4$  concentration. Addition of  $\text{Ce}^{3+}$  to the  $\text{Ce}^{4+}$  solution diminishes the value of  $G(\text{Ce}^{3+})$ . Figure 4 shows the relation between  $G(\text{Ce}^{3+})$  and the concentration of the  $\text{Ce}_2(\text{SO}_4)_3$  added to the solution originally containing  $2\cdot 10^{-4}$  M  $\text{Ce}^{4+}$ , the dosage rate being approximately  $5\cdot 10^{22}$   $\text{ev/ml}\cdot\text{sec}$ ; data from [5] for a dose rate of  $2.5\cdot 10^{15}$   $\text{ev/ml}\cdot\text{sec}$  are also included for comparison.

Our values of  $G(\text{Ti}^{3+})$  at high dosage rates are presented below, each being the mean of 5-12 measurements; from them it is clear this quantity diminishes markedly as the dose rate rises.

Dose rate, $\text{ev/ml}\cdot\text{sec}$	$\sim 10^{21}$	$5\cdot 10^{22}$
$G(\text{Ti}^{3+})$ , ions/100 $\text{ev}$	$1.5 \pm 0.15$	$0.4 \pm 0.2$

According to [5], the mechanism of radiolytic reaction of  $\text{Ce}^{4+}$  and  $\text{Ti}^{3+}$  in 0.8 N sulfate solutions can be expressed by:



\* There was a certain averaging out of the dose rate over the volume of the solution in these experiments. This would not essentially affect the value of  $G(\text{Ce}^{3+})$ .

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It follows that

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$$G(\text{Ce}^{3+})_{\text{Tl}^+} = G_{\text{H}} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} \quad (5)$$

and

$$G(\text{Tl}^{3+}) = G_{\text{OH}} \quad (6)$$

$G_{\text{H}}$ ,  $G_{\text{OH}}$ , and  $G_{\text{H}_2\text{O}_2}$  being the yields of the respective products as obtained in the radiolysis of water.

The present study was set up on the assumption that measurement of the yield from the radiational reactions in the  $\text{Fe}^{2+}$ ,  $\text{Ce}^{4+}$ , and  $\text{Ce}^{4+} - \text{Tl}^+$  systems would permit a quantitative evaluation of the alteration which overlapping of the tracks of the ionizing particles would produce in the yield of radical and molecular products in the water radiolysis. According to [5, 6], at low dosage rates

$$G(\text{Fe}^{3+}) = 3G_{\text{H}} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} \quad (7)$$

for diluted 0.8 N air-saturated aqueous sulfuric acid solutions of  $\text{Fe}^{2+}$  and

$$G(\text{Ce}^{3+}) = G_{\text{H}} - G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} \quad (8)$$

for diluted 0.8 N aqueous sulfuric acid solutions of  $\text{Ce}^{4+}$ . The following expressions can now be obtained from 5, 7, and 8:

$$G(\text{Ce}^{3+})_{\text{Tl}^+} - G(\text{Ce}^{3+}) = 2G_{\text{OH}} \quad (9)$$

$$3G(\text{Ce}^{3+})_{\text{Tl}^+} - G(\text{Fe}^{3+}) = 4G_{\text{H}_2\text{O}_2} + 2G_{\text{OH}} \quad (10)$$

Substitution of our values of  $G(\text{Fe}^{3+})$ ,  $G(\text{Ce}^{3+})$ , and  $G(\text{Ce}^{3+})_{\text{Tl}^+}$  at dosage rates of approximately  $5 \cdot 10^{22}$  ev/ml·sec into these expressions led to negative values of  $G_{\text{H}_2\text{O}_2}$  at all of the investigated  $\text{Tl}^+$  concentrations.

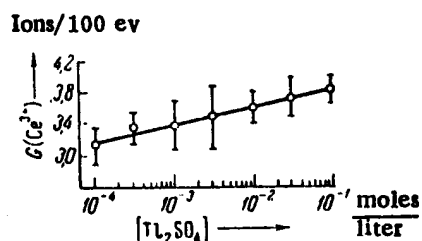


Fig. 3. The relation between  $G(\text{Ce}^{3+})$  and the  $\text{Tl}_2\text{SO}_4$  concentration at a dosage rate of  $4.5 \cdot 10^{22}$  ev/ml·sec ( $\text{Ce}^{4+}$  concentration;  $2 \cdot 10^{-4}$  M).

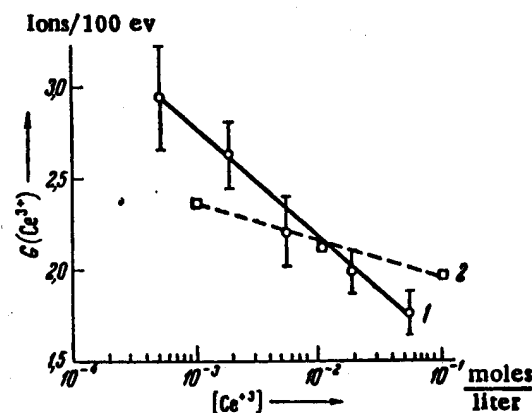


Fig. 4. The relation between  $G(\text{Ce}^{3+})$  and the  $\text{Ce}^{3+}$  concentration at dosage rates of: 1)  $5 \cdot 10^{22}$  ev/ml·sec; 2)  $2.5 \cdot 10^{25}$  ev/ml·sec [5].

\*  $G(\text{Fe}^{3+})$  and  $G(\text{Ce}^{3+})$  had been determined earlier [2, 3].

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From this we assumed that at high dose rates the  $Tl^{3+}$  formed through reaction 3 could either interact with  $Ce^{4+}$  according to reaction 4 or enter into side reactions. Chief among these latter reactions would be the reduction of  $Tl^{3+}$  by hydroperoxide radicals or H atoms:<sup>\*</sup>



or, possibly, reduction by hydrogen peroxide:



Disproportionation of the  $Tl^{3+}$  according to



probably plays a very significant role here since, within the limits of experimental error,  $\frac{1}{2}[G(Ce^{3+})_{Tl^+} - G(Ce^{3+})] = G(Tl^{3+})$ .

It is quite likely that there is a reverse reaction involving  $Tl^{3+}$  and hydrogen peroxide when the dosage rate is high:



or

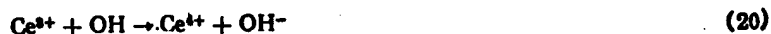


This supposition is confirmed by the fact that the relation between the reduction of  $Ce^{4+}$  in the presence of  $Tl^+$  and the dosage is no longer linear when the dosage is high (see Fig. 2). The role of side reactions of  $Tl^{3+}$  ions in the radiational transformation of  $Ce^{4+}$  in the  $Ce^{4+} - Tl^+$  system is a minor one for irradiation at low dosage rates.

The increase in  $G(Ce^{3+})$  with increasing  $Tl^+$  concentration is clearly to be explained in terms of a competition between reactions (3) and (16) and (17):<sup>\*\*</sup>



In all likelihood, the decrease of  $G(Ce^{3+})$  with increasing  $Ce^{3+}$  concentration is the result of a competition between (19) and



just as is the case at low dosage rates [5].

<sup>\*</sup> This reaction clearly leads to a reduction in the value of  $G(Ce^{3+})_{Tl^+}$ .

<sup>\*\*</sup> The significance of reactions (16) and (17) for radiolytic transformations in aqueous solutions increases markedly at high dosage rates where there is overlapping of the tracks of the ionizing particles, and the same is true of:

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It should be noted that the relation between  $G(\text{Ce}^{3+})$  and the  $\text{Ce}^{3+}$  concentration is most clear-cut at the high dosage rates. Curves covering these relations at dose rates of approximately  $5 \cdot 10^{22}$  and  $2.5 \cdot 10^{18}$   $\text{ev/ml} \cdot \text{sec}$ , respectively, intersect. From a  $\text{Ce}^{3+}$  concentration of approximately  $10^{-2}$  M on, the  $G(\text{Ce}^{3+})$  value for a dose rate of approximately  $5 \cdot 10^{22}$   $\text{ev/ml} \cdot \text{sec}$  is greater than the corresponding value for a dose rate of  $2.5 \cdot 10^{18}$   $\text{ev/ml} \cdot \text{sec}$ . Thus, it is necessary to introduce about  $10^{-2}$  M of a  $\text{Ce}^{3+}$  salt into a solution containing  $\text{Ce}^{4+}$  in order to suppress the formation of those additional quantities of  $\text{H}_2\text{O}_2$  which would result from (19) by overlapping of the tracks of ionizing particles. At  $\text{Ce}^{3+}$  concentrations in excess of  $10^{-2}$  M, the principal alteration in  $G(\text{Ce}^{3+})$  at high rates of dosage is that due to the diminution of  $G_{\text{H}}$  resulting from the overlapping of the tracks of the ionizing particles.

Thus, competition between radical-radical and radical-dissolved substance interactions, and side reactions between the intermediates, become increasingly significant to transformations in aqueous solutions as the dosage rate is increased and the radical concentration rises.

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\* Original Russian pagination. See C. B. translation.

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